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KINETIC OF SORBITOL DECOMPOSITION UNDER NON-ISOTHERMAL CONDITIONS

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The thermal behavior of sorbitol was studied under non-isothermal conditions, in both air and nitrogen atmosphere. The main process is a deep and continuous dehydration.

For the kinetic analysis, the TG/DTG data obtained at five heating rates were processed by three different methods: Friedman, Budrugeac–Segal and non-parametric kinetic, respectively. This analysis indicates a complex reaction with a preponderant chemical process, described by a conversion function $(1-\alpha)^{3/2}$, accompanied by diffusion.

Keywords: *Budrugeac–Segal method based on compensation effect, food additives, isoconversional methods, non-isothermal kinetics, NPK method, sorbitol*

Introduction

Sorbitol and its derivatives are widely used in the food industry [1]. In order to protect the customers, it is of a real interest the thermal stability of such food additives, taking into account that in the baking process of different daily products, the tempertures can reach 350°C [2].

In some previous papers [3–6] the kinetic data obtained under non-isothermal conditions were used for appreciate the thermal behavior of some pharmaceuticals and food additives.

The aim of this paper is to investigate the kinetics of thermal decomposition of sorbitol in both air and nitrogen atmosphere, under non-isothermal conditions. The data processing is similar with that presented in our recent papers [7–9].

Experimental

The studied sorbitol sample was a commercial product [10].

The thermal behavior was first tested on a MOM Q-1000 Derivatograph in static air atmosphere with a Pt crucible and a heating rate of 2.5 K min^{-1} in the range 25–500°C.

For the kinetic studies, the thermogravimetric (TG) curves were obtained on a Perkin-Elmer TGA7 device using a Pt crucible, dynamic nitrogen atmosphere and heating rates (β) of 2.5, 5, 7, 10 and 12 K min^{-1}.

Results and discussion

Thermoanalytical data

The recorded curves obtained on Derivatograph MOM are depicted in Fig. 1.

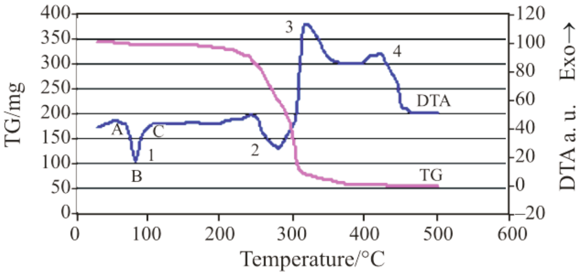
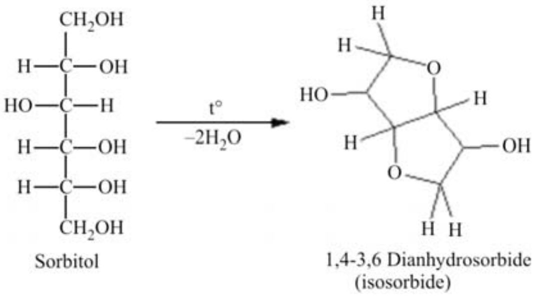


Fig. 1 The TG/DTA curves obtained for a heating rate of 2.5 K min^{-1}

By correlations between the calculated mass loss and the experimental TG curve, the first dehydration process, corresponding to a mass loss of 19.8%, is complete at 250°C, and is assigned to the formation of isosorbide (Eq. (1)).



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In Fig. 2 typical TG/DTG curves obtained in nitrogen atmosphere are presented. The curves recorded in dynamic atmosphere presents a single degradation process, and in absence of oxygen this one is a continuous and severe dehydration.

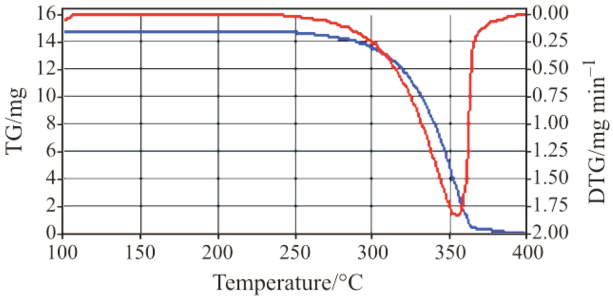

Fig. 2 The TG and DTG curves obtained for a heating rate of 5 K min^{-1}

From TG data the conversion (α) *vs.* temperature (*T*) diagram were regenerated and presented in Fig. 3.

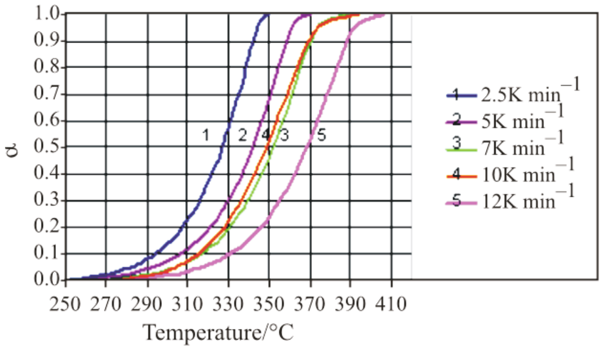

Fig. 3 Conversion variation at 5 different heating rates

The influence of heating rate is obvious.

The endothermic process ABC of the DTA curves (Fig. 1) corresponds to the melting of sorbitol. The mass loss according to TG curve, is about 91% in the range 211–360°C. The main process is dehydration, corresponding to the maximum 2 of the endothermic peak of DTA, respectively to the maximum of the DTG curve.

After dehydration, the degradation is continued by oxidation processes, observed by the exotherm peaks 3 and 4 of the DTA curve.

Kinetic analysis

We began the kinetic analysis with the Friedman's differential isoconversional method [11], using the relationship pointed below:

$$\ln\left(\beta\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)=\ln[A(\alpha)]-\frac{E}{R}\frac{1}{T} \tag{2}$$

where α – conversion degree, β – heating rate, *A* – pre-exponential factor and *E* – activation energy in sense of Arrhenius equation.

With α constant and various heating rates, the plot of the left member of Eq. (2) *vs.* 1/*T* should be linear, and from the slope the value of activation energy was calculated and is presented in Table 1.

In Figs 4 and 5 the experimental data are presented in a suitable form for processing.

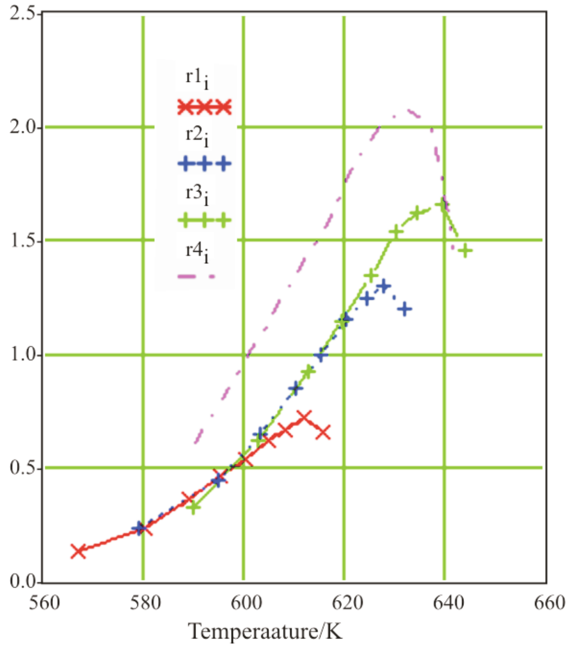

Fig. 4 Reaction rate *vs.* temperature

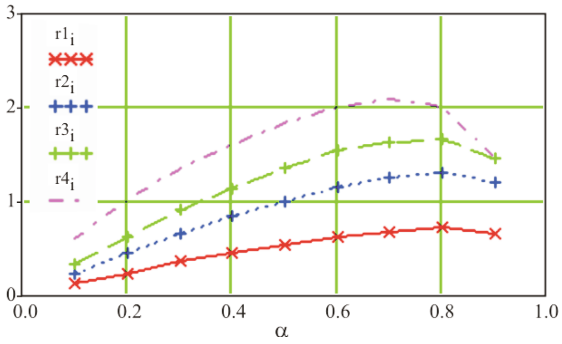

Fig. 5 Reaction rate *vs.* conversion

From the data in Table 1, a significant variation of *E* *vs.* α was observed, this being a sign of a complex process.

Therefore, we have continued the kinetic analysis with the Budrugeac–Segal method [12–14] based on the following assumptions:

- *E* and *A* depend on the conversion degree and not on the heating rate;
- *E* and *A* are correlated through the compensation effect

Table 1 Activation energy (E) obtained by Friedman's method for heating rate of 2.5, 5, 7, 10 and 12 K min^{-1}

α	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
E/ kJ mol^{-1}	154.5 ±44.7	160.8 ±49.1	147.1 ±43.3	139.7 ±36.0	136.7 ±38.4	132.8 ±31.8	126.6 ±25.7	112.1 ±19.3	95.7 ±11.8

Table 2 Kinetic parameters of the compensation effect according to Eq. (7)

	E_0/kJ mol^{-1}	E_1/kJ mol^{-1}	a	b	n	Corr. coef.
Sorbitol	158.6±52.3	27.9±2.2	$1.95\cdot10^{-4}\pm0.01\cdot10^{-4}$	–1.18±0.52	0.9	0.9994

$$\ln A=aE+b \tag{3}$$

- the dependence E *vs.* α is described by:

$$E=E_0+E_1\ln(1-\alpha) \tag{4}$$

where E_0 and E_1 are constants.

- the differential conversion function, $f(\alpha)$ it take the form:

$$f(\alpha)=(1-\alpha)^{\mathrm{n}} \tag{5}$$

From Eq. (5) it results:

$$\ln[Af(\alpha)]=\ln A+n\ln(1-\alpha) \tag{6}$$

and from the value of the product $[Af(\alpha)]$ and α it can be obtained ln$A$, which is corresponding to different values of n. The plot ln$A$ *vs.* E should be linear for a compensation effect.

All these hypothesis lead to the Eq. (7).

$$\ln\left(\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)=\left(b+aE_0-\frac{E_0}{RT}\right)+\left(aE_1-\frac{E_1}{RT}+n\right)\ln(1-\alpha) \tag{7}$$

from which, the kinetic parameters systematized in Table 2 were obtained.

In Fig. 6 the expected compensation effect according to Eq. (3) is depicted.

In order to obtain more details about the kinetic of this complex process we have used the NPK method [15–17]. This method is based on the assumption that the reaction rate can be expressed as a product of two independent functions, $g(\alpha)$ and $f(T)$.

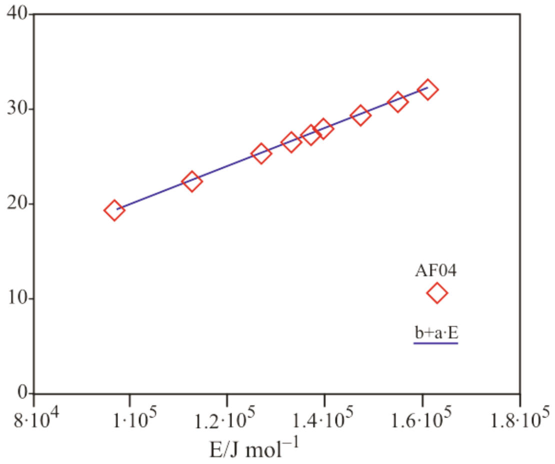

Fig. 6 The compensation effect

The reaction rate dα/dt, measured from several experiments, carried out at different heating rates β, are represented in a 3D space (α, T, α(dα/dT)) and interpolated as a continous surface of the reaction rate, corresponding to the equation.

$$\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}=f(\alpha)g(\alpha) \tag{8}$$

From this surface, a square matrix M is generated; its rows correspond to different degrees of conversion, from α_1 to α_i and its columns correspond to different reaction temperatures, from T_1 to T_i.

The NPK method uses the singular value decomposition (SVD) algorithm to decompose the matrix in two vectors describing the variation of the reaction rate due to the temperature and conversion, respectively.

For the function $f(T)$, a classical Arrhenius equation was used, and for the kinetic model $g(\alpha)$, the Šesták–Berggren [18] equation was proposed:

$$g(\alpha)=\alpha^{\mathrm{m}}(1-\alpha)^{\mathrm{n}} \tag{9}$$

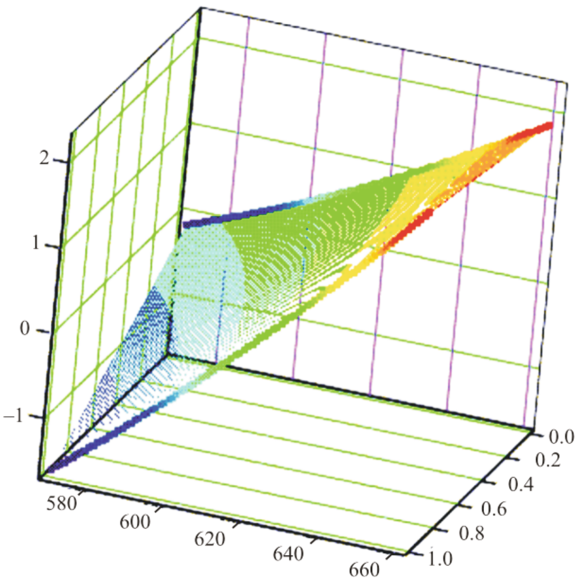

Fig. 7 The surface of the reaction rate in a 3D space

Table 3 NPK kinetic parameters for preponderant and secondary process

	E/kJ mol^{-1}	A/min^{-1}	λ/%	n	m	Šesták–Berggren eq.
Preponderant process	99.8±6.3	$7.4\cdot 10^{7}\pm 3.2$	89.9	3/2	1	$(1-\alpha)^{3/2}\,\alpha^{1}$
Secondary process	343.0±53.4	$2.8\cdot 10^{27}\pm 2.4\cdot 10^{4}$	10	–	2	α^{2}

By our experimental data, the initial generated matrix M has been decomposed in two matrix:

$$M=M_1+M_2 \qquad (10)$$

It means that they are two processes, the contribution of each process to the decomposition reaction being characterized by the explained variance λ ($\lambda_1+\lambda_2=100\%$).

The data of the kinetic analysis by the NPK method are systematized in Table 3.

Because the explained variance (λ) is around 90% we can say that the secondary process observed could be negligible. This means that, indeed, there is a complex process, the first one a chemical process, n=3/2 accompanied by diffusion, m=1, the secondary, only a physical process, m=2.

Conclusions

By the thermal decomposition of sorbitol, the main process is a deep and continuous dehydration in melted state.

Data processing with three different methods, i.e. Friedman, Budrugeac–Segal and NPK, indicates a complex process with a preponderant chemical respectively a secondary physical step. Also the existence of a compensation effect was observed.

The NPK method allows a more realistic kinetic analysis of thermogravimetric data of complex processes.

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